

South Africa, have an excess of light carbon in the reduced carbon. Incidentally, we don't really know when the earth was put together. All we can do is try to date the rocks, and the sedimentary rocks that we have are about as old as the oldest igneous rocks that have been dated.

The evidence, in other words, is that we had something pretty complicated going very quickly.

DR. CLOUD: That is all the discussion we have time for on this paper.

*HISTORY OF MAJOR ATMOSPHERIC COMPONENTS**

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We postulate the initial premise that upon its formation the earth accumulated without an external primordial atmosphere. This postulate seems established by the very high fractionation ratios of the noble gases, following Harrison Brown (1949) (e.g., terrestrial neon/silicon abundance $\sim 10^{-10}$ compared to its universal ratio), and by the relatively large loss of hydrogen and helium by the inner planets (A. P. Vinogradov, 1959). For example, the terrestrial fractionation ratio of Ne to N, which are similar in atomic weight, with respect to their comparable abundances in the universe (universally Ne/N $\sim 8.6/6.6$) is of the order of one millionth. This leads to the direct implication that those atmospheric constituents which were not bound chemically in solids of the planetesimals forming the earth were lost from their low gravitational fields prior to their agglomeration into the earth.

This postulate leads to the view that the atmospheric gases of the earth are of secondary internal origin. Following Rayleigh (1939), Rubey (1951, 1955), and others, the major and significant juvenile source of atmospheric gases (excepting only oxygen) is volcanic action. Atmospheric and fossil quantities of atmospheric gases and water appear consistent over geologic time with volcanic effluents of H_2O , CO_2 , N_2 , H_2 , etc., as well as with the solid lava materials which have formed the continents and with which the gaseous effluents were presumably associated in juvenile form. For example, quantitative examination of nitrogenic compounds in the rocks indicates differentiation of from 5 to 50 times the quantity of mantle materials in the magmatic processes producing the crust and the juvenile nitrogen of the atmosphere, together with its fossil counterpart (see Lord F. R. S. Rayleigh, 1939). The work of Urey (1952) shows from the physical chemistry of the earth that its magma was selectively molten—probably not wholly molten during any geologic period—so that juvenile volcanic effluents were discharged more or less uniformly over the ages.

Oxygen appears to be largely absent from the primitive secondary atmosphere. Oxygen is not present in volcanic effluents, and any available oxygen in such effluents would be lost in oxidation processes associated with volcanoes (H. D. Holland, 1962). Partial oxidation of very early rocks is consistent with such low oxygenic levels, according to MacGregor (1940), Lepp and Goldich (1959), and Rutten (1962). Moreover, oxygen in significant quantities is toxic to the primitive

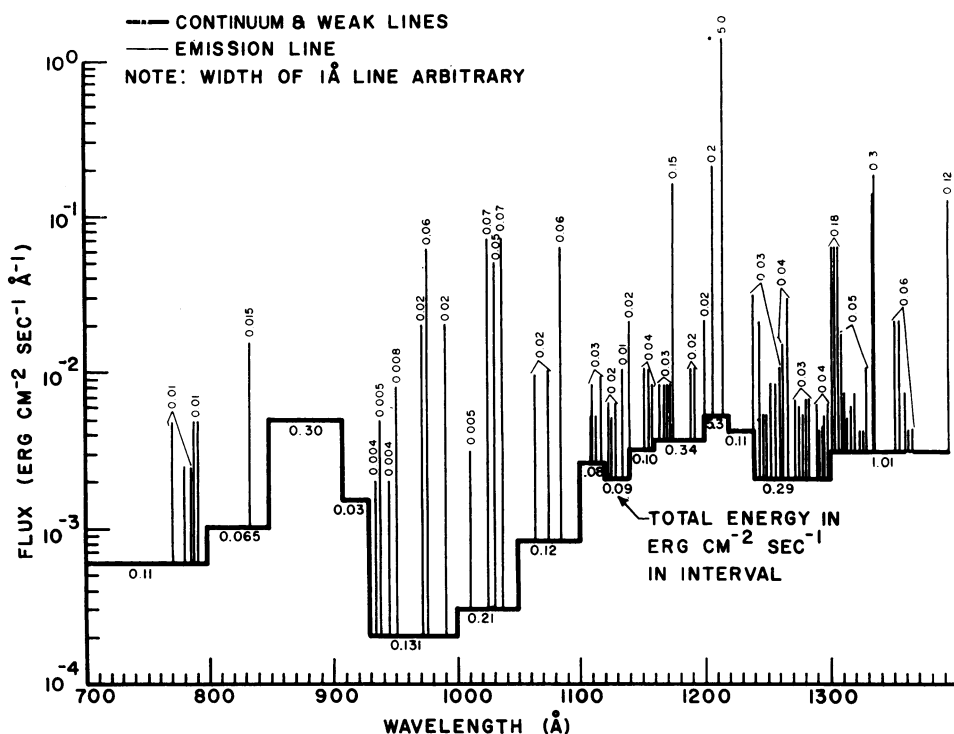


FIG. 1.—Solar intensity, 700–1400 Å (composite data from P. J. Nawrocki and R. Papa).

organic materials from which life must have been organized (cf. P. H. Abelson, 1957). Only in advanced cellular organisms are developed the enzymes employing vitamins to create oxygenic defenses (see D. L. Gilbert, 1964). Finally, all free atmospheric oxygen must be derived from H_2O by photodissociation or photosynthesis. Prior to life, and absence of significant ocean areas, the sources of oxygen were small, and its consumption by surface oxidation through ozone as

shown later is large, so that equilibrium levels would be low.

In 1959, Urey suggested that oxygen production in the primitive atmosphere by photodissociation of H_2O would be restricted and self-regulated since the oxygen so produced would shadow the underlying water vapor, thereby bringing photodissociation to a halt. Berkner and Marshall (1964, 1965) have calculated the primitive restriction on oxygenic concentration imposed

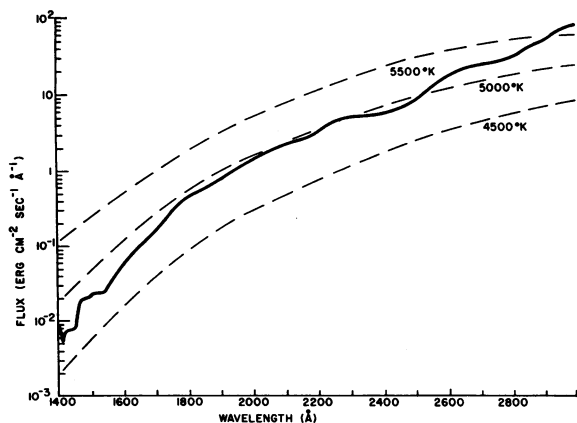


FIG. 2.—Solar intensity, 1400–3000 Å (composite data from P. J. Nawrocki and R. Papa).

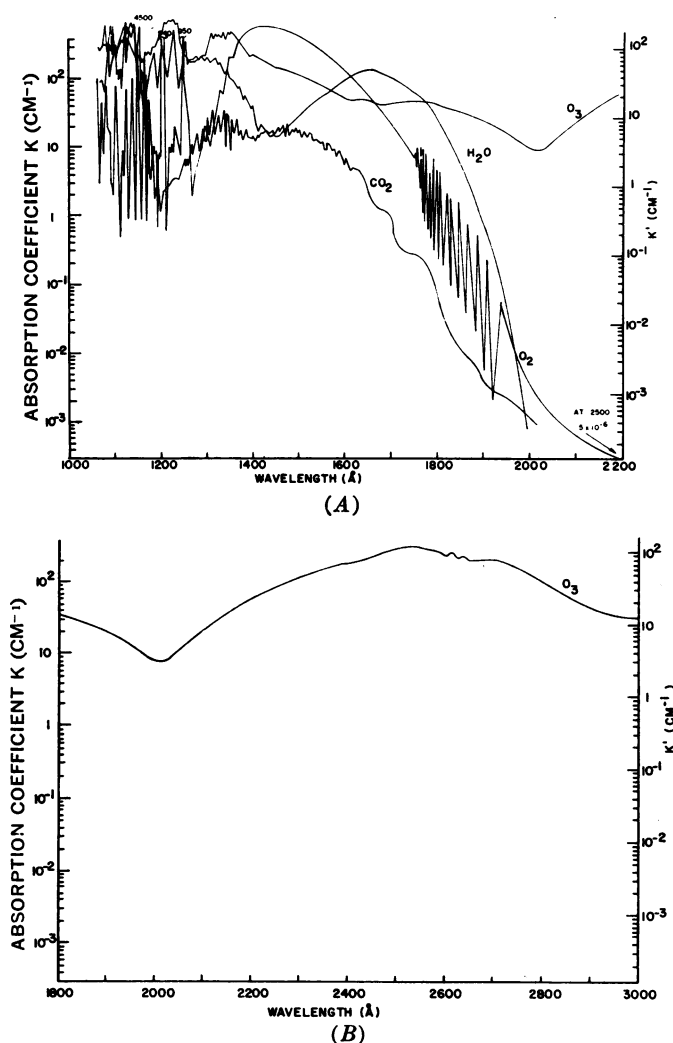


FIG. 3.—(A) Composite of UV absorption in atmospheric gases; (B) UV absorption in O₃ (data from K. Watanabe and E. Vigroux).

by this “Urey effect” (Figs. 1 and 2). The distribution of solar radiation in the UV bands is now well known, as a consequence of measurements by rockets and satellites, and summarized by Nawrocki and Papa (1961).

The significant proportion of UV involved in photodissociation of major atmospheric components (99.9%) lies above 1400 Å. This radiation arises from the sun’s photosphere and is relatively stable as contrasted to the strong line radiation from the chromosphere corona at shorter wavelengths. From the study of M-type stars, Wilson (1963) suggests that such photospheric radiation will not vary by as much as a factor of 3 over geologic time. Therefore, the sun’s UV radiation between 3000 and 1400 Å can be assumed as constant over geologic time. Watanabe and his colleagues (1953, 1959) and Vigroux (1953) have measured the absorption of this radiation (Fig. 3) over the UV band for all significant atmospheric constituents.

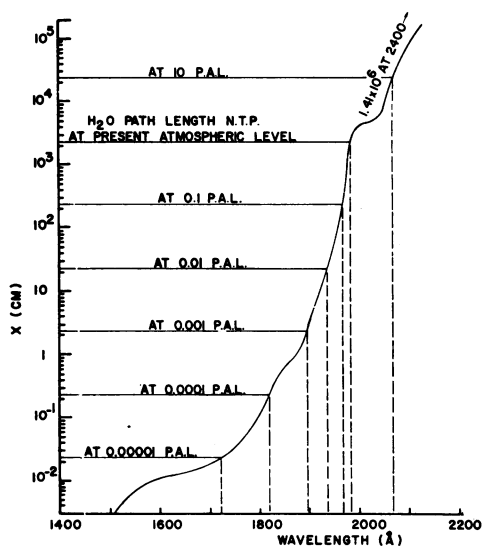


FIG. 4.—Thickness of H_2O required to absorb available UV to "extinction" [$1 \text{ erg cm}^{-2} \text{ sec}^{-1} (50 \text{ Å})^{-1}$].

Because of the cold ceiling of the tropopause, H_2O is not distributed exponentially with height, while the O_2 produced by photodissociation of H_2O is exponentially distributed. Consequently, when the path length of O_2 reaches 35 cm above an altitude of 10–12 km, the H_2O of the troposphere is effectively shadowed from dissociative UV, bringing photodissociation of H_2O to a halt. Since 35 cm path length of O_2 at 10 km corresponds to an oxygenic level $<10^{-3}$ present atmospheric level (P.A.L.), Berkner and Marshall conclude that the oxygen in the primitive atmosphere was regulated at less than 0.1 per cent present concentration. Taking atmospheric

Thus, data on solar radiation and its absorption can be combined at each wavelength to ascertain the N. T. P. path length for each wavelength to an arbitrarily defined energy level, say, $1 \text{ erg cm}^{-2} \text{ sec}^{-1} (50 \text{ Å})^{-1}$ (Fig. 4).

We observe that the path length through H_2O vapor at its present atmospheric concentration reduces the UV energy level to this value at 1950 Å (and below this energy level at shorter wavelengths), with the cutoff very insensitive to pressure, due to the steep rise of its curve for UV absorption (Fig. 5). On the other hand, O_2 at this wavelength requires only 35 cm path length to absorb to this energy level at 1950 Å, and strongly overlaps the H_2O absorption everywhere over the UV range (Fig. 6).

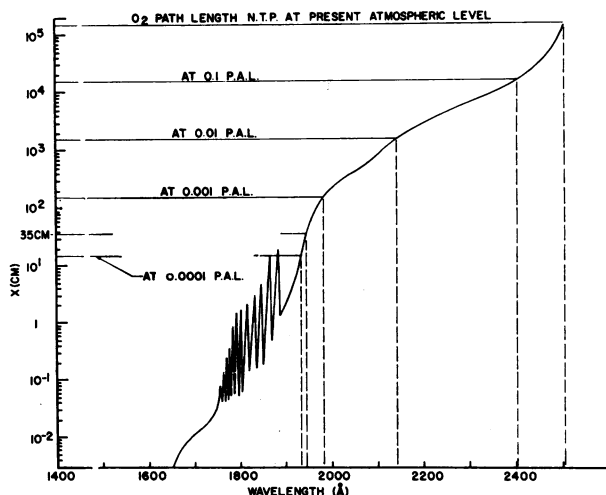
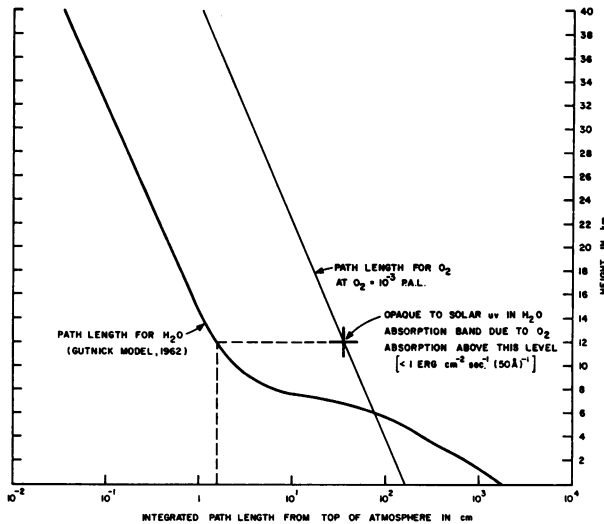


FIG. 5.—Thickness of O_2 required to absorb available UV to "extinction" [$1 \text{ erg cm}^{-2} \text{ sec}^{-1} (50 \text{ Å})^{-1}$].

FIG. 6.—Shielding from photodissociation of atmospheric H_2O by O_2 .

CO_2 into account would lower this primitive level somewhat, for its absorption curve lies below those for H_2O and O_2 , and its concentration (W. W. Rubey, 1951) is limited by precipitation of carbonates in water.

With respect to other possible constituents, CO is not stable in an atmosphere containing O and O_3 , which react at moderate temperatures and react strongly in presence of UV, going to CO_2 . NH_3 is highly soluble and chemically active, being substantially removed in presence of water. According to Nicolet (1964), the very small quantities of H_2O above the tropopause can produce no net amounts of O_2 by photodissociation because of the photodissociation of equivalent quantities of CH_4 by wavelengths shorter than 1200 \AA , and reaction of its elementary components with oxygen atoms. In any event, photodissociation of the small quantities of water vapor above the tropopause could not bring O_2 above the self-regulated concentration because of the rates of loss through ozone, as will be shown later.

The low concentration of oxygen in the early atmosphere, as it rises to the self-regulated limit of $< 10^{-3} \text{ P.A.L.}$, has interesting consequences in oxidation of rocks during the intermediate ages (Fig. 7). The height of maximum production of ozone will be lowered by one scale-height for each decimal reduction in oxygen concentration due to corresponding lowering of the altitude of production of oxygen atoms. The concentration of ozone at the level of

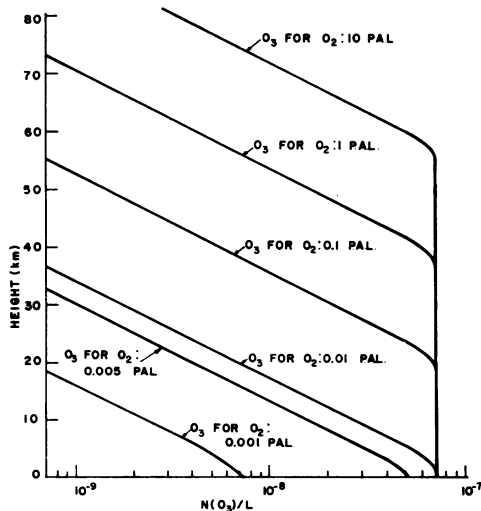


FIG. 7.—Estimated idealized distribution of ozone for various levels of oxygen.

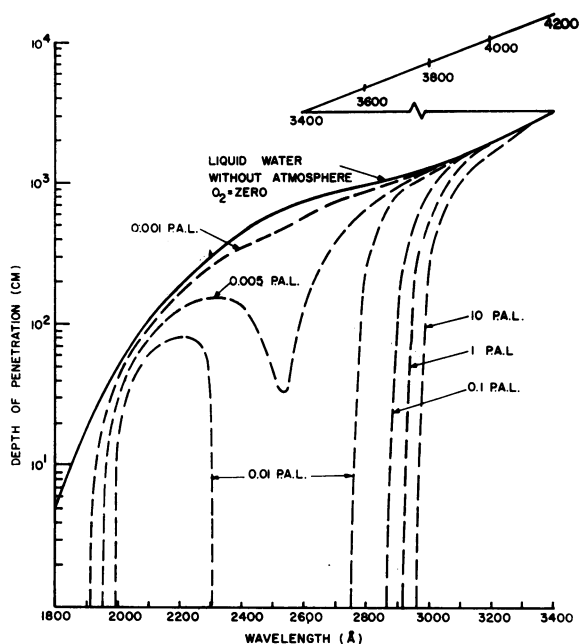


FIG. 8.—Path length in liquid water in presence of O_2 and O_3 for various concentrations of O to absorb available UV to "extinction" [$1 \text{ erg cm}^{-2} \text{ sec}^{-1} (50 \text{ Å})^{-1}$].

production of O will vary as a function of temperature and total pressure because of the process of three-body collision involved in its formation.

The highly stylized representation of Figure 7 illustrates the character of ozone distribution, assuming total pressure proportional to partial pressure of oxygen. At higher total pressures (most probably due to higher concentrations of nitrogen, which is the obvious candidate for the third body in the reaction), the concentrations (but not the altitudes) of ozone would be somewhat increased. A considerable range of atmospheric assumptions relative to atmospheric characteristics controlling ozone production would elaborate, but not substantially modify, the quality of subsequent conclusions.

As a result, in the primitive and intermediate atmospheres, atomic oxygen and ozone will be produced in a thin layer in contact with the earth's surface. Since reaction rates of both O and O_3 are many orders of magnitude times the reaction rates of O_2 , with respect to surface materials, the loss of O and O_3 as surface oxidants represents the principal loss of oxygen. Thus, even in the early tenuous oxygenic atmospheres, surface oxidation rates could well have exceeded present values considerably. Berkner and Marshall have computed total UV energy available over geologic time and find it adequate by this process to account for all fossil oxygen with quantum efficiencies for photodissociation of O_2 of less than 1 per cent. Thus the frequent assumption that crustal oxides in the early and intermediate ages require high atmospheric oxygen concentration becomes unnecessary.

As a further consequence of the production of ozone at the earth's surface in early atmospheres, we can now state that to build an oxygenic atmosphere, the rate of production of O_2 must exceed its rate of photodissociation and consequent loss.

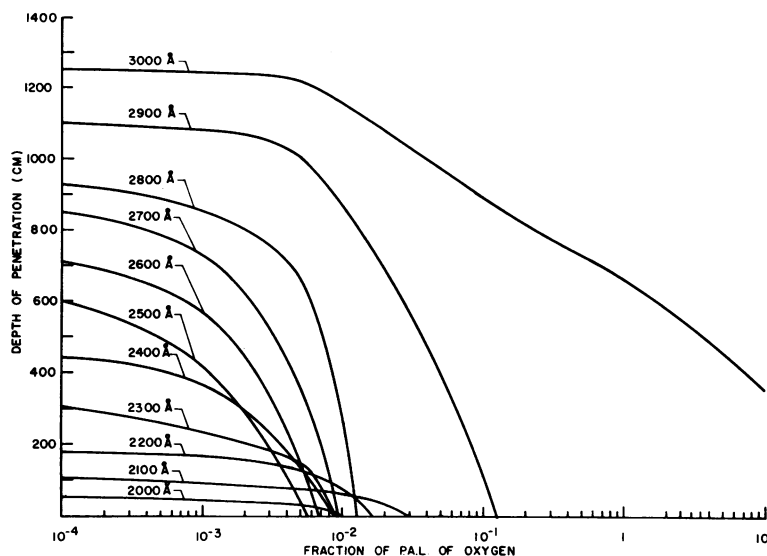


FIG. 9.—Penetration of UV in liquid water with various combinations of oxygen and ozone atmospheres [intensity at extinction = $1 \text{ erg cm}^{-2} \text{ sec}^{-1} (50 \text{ Å})^{-1}$].

Only under this condition can the self-regulated equilibrium of oxygenic levels be upset, since the increase of oxygen concentration can only arise from a small positive differential between the relatively larger processes of production and of removal.

We therefore inquire into the restrictions on photosynthesis in the presence of the early atmosphere. Figure 8 illustrates the penetration of UV into water, through the atmosphere defined in Figure 7, to a peak intensity of $1 \text{ erg cm}^{-2} \text{ sec}^{-1} (50 \text{ Å})^{-1}$. This defines the early ecology, in approximate consonance with Sagan's estimates (1957, 1961), to bottom-dwelling organisms in about 10 meters of water. The environment must be protected by sufficient depth of water to protect from lethal UV, but sufficiently shallow to maximize photosynthesis, with gentle convection to supply nutrients but no violent convection that would circulate primitive benthic organisms (having no advanced forms of control) toward the lethal surface. Thus, primitive photosynthetic life must be restricted to shallow lakes or shallow protected seas. The early bioherms described by Hoering and Abelson (1961) as supporting living organisms in the era —2.7 billion years appear prime seats for the origin of life. In particular, pelagic life in the oceans appears forbidden. Of particular interest, we observe that nucleic acids, proteins, and other essential elements for life, whose maximum absorption of UV falls between 2400 and 2800 Å, have the most favorable opportunity for natural selection. This appears as a basic characteristic of our solar system.

In this ecology, we make the preliminary estimate that photosynthetic organisms at present densities must cover somewhat more than 1 per cent of present continental areas to upset the Urey self-regulated equilibrium and begin the construction of an oxygenic atmosphere (Fig. 9).

Reorganizing the data of Figure 8, we observe that as oxygen rises to 1 per cent P.A.L. the penetration of lethal UV is confined to a thin layer of surface water, opening

life to the oceans. Moreover, at this oxygenic level, many organisms pass the "Pasteur point," adapting their metabolism from fermentation to respiration, thereby increasing available metabolic energies per gram-mol by about 50 times. With the appearance of respiration, evolutionary requirements appear for a nervous system to control the process, a circulatory system for oxygen distribution, a digestive system to maximize it, and so on. With the evolutionary opportunities offered by respiration and its consequences, and the extensive isolation offered by opening the oceans to pelagic life, one can anticipate an evolutionary explosion toward more complex organisms when $O_2 \rightarrow 10^{-2}$ P.A.L.

We therefore inquire from the geologic record whether such an evolutionary explosion occurred. There is just one—the opening of the Paleozoic, 6×10^{-8} years ago. By immediate inference, Berkner and Marshall identify the opening of the Paleozoic with the oxygenic level, $O_2 \sim 10^{-2}$ P.A.L. (see L. V. Berkner, 1952). Following this model, the geologic record should be read exactly as observed, with no long interval of advanced evolutionary development interpolated prior to the opening of the Paleozoic.

In a critical study and review of geologic, paleontologic, and geochemical evidence during the Pre-Cambrian, which has just appeared, Cloud (1965) reaches several conclusions which bear strongly on this model.

(1) There is clear paleontologic evidence of early thallophyta, some probably oxygen-producers, as early as 1.9 billion years ago.

(2) (Cloud makes the interesting suggestion that): Local and isolated centers of biological oxygen production, in some kind of dependent balance with dissolved ferrous ion as an oxygen acceptor, can account for the different ages and facies of Pre-Cambrian-banded iron formation in different parts of the world, this process at the same time inhibiting oxygen release, into an essentially anoxygenic atmosphere.

(3) There is no evidence of multicellular organisms prior to the opening of the Cambrian. The beginning of the Paleozoic should be "defined operationally as the base of the range-zone of Metazoa (or Eumetazoa if we exclude the sponges)."

(4) "By the beginning of Paleozoic time, about 0.6 billion years ago, enough oxygen had accumulated to permit evolution and diversification of the Metazoa."

These conclusions are in general consonance with the Berkner-Marshall model, with any question of dating hinging on the speed of response of metazoan evolution to the evolutionary niches opened by respiratory opportunity. Thus, Cloud, on geologic reasoning, would leave open the dating of the 1 per cent of present oxygenic level between the limits of 1.2 billion years and the Berkner-Marshall inference of 0.6 billion years. The Berkner-Marshall model would question the admissibility of this span, since as $O_2 \rightarrow 10^{-2}$ P.A.L. the expansion of even primitive unicellular photosynthetic activity would lead to a more rapid rise in oxygenic concentrations during this period than can be inferred from the subsequent succession of events. Certainly, further critical examination of this detail of the model will be made.

With the evolutionary explosion of the earlier Paleozoic, photosynthetic production of oxygen is materially increased. We then observe from Figure 9 that as oxygen approaches 0.1 P.A.L., the land surface is just protected from lethal UV, opening the evolutionary opportunity ashore. Definite spores of land plants appear first in mid-Silurian, suggesting that spore-bearing plants could then first

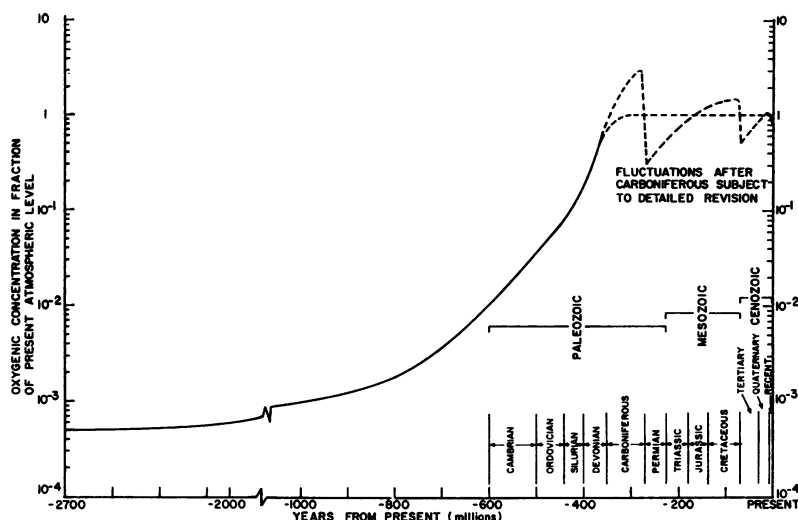


FIG. 10.—Model of oxygenic evolution.

stick their heads above water without lethal sunburn. Immediately, in late Silurian, a number of phyla of plants and insects appear to have evolved ashore simultaneously, with great forests found by early Devonian. At the same time, the advanced respiratory apparatus of the fishes was developed, an apparatus requiring higher oxygenic levels. Almost immediately, vertebrate life evolved ashore.

By immediate inference, the Berkner-Marshall model identifies the oxygenic level $O_2 \sim 10^{-1}$ P.A.L. with the late Silurian evolution of life ashore.

With the explosion of life ashore, photosynthetic production of O_2 is increased some 20 per cent, further altering the oxygen balance and promoting rapid rise of O_2 toward the Carboniferous. Because the production of CO_2 due to decay of organic materials may have lagged in phase behind the rise in production of O_2 , some fluctuation in O_2 can be anticipated in subsequent geologic periods. More particularly, any induced climatic change that deadapts specialized photosynthetic producers in substantial numbers, thereby upsetting the oxygen balance, can cause a precipitous drop in O_2 concentration due to successive deadadaptation as oxygen falls, followed by a slow recovery as new organisms are readapted. The present quasi-stable oxygen concentration involving a rate of O_2 production of 7×10^{13} molecules $cm^{-2} sec^{-1}$ over the earth corresponds to a lifetime of atmospheric oxygen of only some 2000 years until its return through the biological cycle—a time negligibly short compared to geologic periods (see Rabinowitch, 1951). Consequently, fluctuations in oxygenic levels introduced by precipitous drops in oxygenic concentrations followed by slower recovery can be expected in the late Paleozoic and subsequent periods.

Summarizing the best estimates of oxygenic concentration in the several ages, Berkner and Marshall arrive at the model illustrated in Figure 10. We believe this represents the most logical synthesis of available information and it provides a model of considerable self-consistency of a very wide range of observations. It is,

of course, open to refinement as new data are acquired and their meaning is adduced.

In conclusion, we must observe that the present work on paleoatmospheres opens a new vista in the understanding and description of major features of the successive geologic periods, particularly since the Cambrian. Specialized geologic features (such as the widespread red-beds of the Devonian or Permian, for example) might be related to the oxidizing characteristics of the atmosphere, i.e., the concentrations of O and O₃ and, through either surface-production or convection, their relative access to the surface iron, sulfur, and other reduced or partially oxidized materials. The oxidizing character of the atmosphere in any geologic period in turn depends not merely on oxygenic levels, but also on inferred concentrations of third bodies such as nitrogen and carbon dioxide, and on the consequent temperature and altitude of the ozone-producing layer. The conclusion of Hutchinson (1944) that nitrogen has increased through geologic time probably uniformly, to a first approximation, and of Rubey (1951, 1955), concerning concentrations of CO₂, provides the preliminary basis for commencing such quantitative studies. As the level of production of O and O₃ rises through the present troposphere, the temperature at and above the present tropopause will be changed violently, with first superadiabatic and then less than adiabatic lapse rates in the troposphere thus changing convective activity completely from one period to another. The estimates of atmospheric composition in successive geologic periods can be controlled by the requirement that the atmospheric changes between successive geologic periods must lead to a self-consistent succession of atmospheric events.

Moreover, such models raise altogether different and critical paleontological questions that can guide the search for new and related evidence.

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(Discussion of Berkner-Marshall paper)

DR. HANS SEUSS (University of California, San Diego): I would like to make a comment on the self-regulating Urey mechanism for production of oxygen by photolysis. I don't think you can give a lower limit for the oxygen that remains behind hydrogen after photolysis takes place. We now still have hydrogen in the atmosphere, and I have shown almost 20 years ago that this hydrogen is produced by photolysis in the upper atmosphere. Hydrogen escapes from the earth's gravity field today. It is easy to calculate that the rate by which it leaves is not sufficient to produce all the oxygen present now in the atmosphere, but it is certainly higher than the limit you gave.

Of course, the rate and the amount of hydrogen that is produced by photolysis is related to the oxygen in the atmosphere, but we don't know what the relation is and, therefore, we cannot give any quantitative values for how much of the oxygen was produced by photolysis. Certainly, of the present amount, a large amount is determined by photosynthesis, but to divide it up as to which is produced by photolysis and which is produced by plants is quite impossible.

DR. BERKNER: I would refer you to a paper by Nicolet in 1964 which analyzes precisely the process you discuss. You will remember from Figure 6 that above a height of about 10 kilometers only one centimeter path length of hydrogen or less remains. Nicolet points out that because of the photodissociation of CH₄ in the

outer atmosphere, in the presence of oxygen atom, there will be a net production of water vapor in the outer atmosphere and not a loss. Therefore, photolytic production in the outer atmosphere from H_2O as a source of oxygen is not a valid source in the primitive nor in the present atmosphere.

DR. SEUSS: I discussed this with Nicolet. He was not quite familiar with the studies we made on the isotropic conditions as they are now. These were the only measurements that were made.

DR. BERKNER: Since only one centimeter of hydrogen is available above the level shielded by oxygen in the primitive atmosphere, the total numbers of quanta absorbed in the high atmosphere by H_2O for the production of O_2 are too small to bring O_2 above the self-regulated level in light of the losses of O_2 . I have this in the paper, but I skipped it in reading.

DR. COMMONER: It is pertinent to mention that ozone is rather toxic.

DR. BERKNER: When ozone dissolves in water, it forms O_2 . Some have suggested H_2O_2 might be formed, and I believe Urey mentioned this in his paper this morning. It will not remain as O_3 . In the primitive atmosphere ozone must be in contact with the surface. In the most primitive atmosphere for which we estimated the ozone levels, as you will recall from Figure 7, the ozone levels are very low indeed. There is enough to provide for surface-oxidation processes due to the atmosphere. As for the actual quantities of ozone, when you get down to 5×10^{-4} of the present oxygenic concentrations, the ozone level is far lower than it is even in the present stratosphere. It is only as you come above the 10^{-3} level of present oxygenic concentration that ozone tends to be comparable in density to the present stratospheric levels.

I will say that if nitrogen had a higher pressure in the early ages than Hutchinson predicts, then the ozone levels would be a little higher—not very much, because ozone rises as a function of total pressure.

DR. CLOUD: Our time is up. I must thank the speakers for adhering beautifully to their time so that we could come out right on schedule. The symposium stands adjourned.
